

## Chemical Compound Classification by Elemental Signatures in Castle Dust Using SEM Automated X-ray Particle Analysis

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Discoloration on the Smithsonian Institution Building (1847-1855) and Enid A. Haupt Garden gateposts (1987) was recently revealed to be related to a Mn enriched rock varnish [1]. Mn does not appear to be derived locally from the building stone; therefore, its source is likely related to atmospheric dust transport. Minor oxygen isotopic ratios ( $\delta^{17}\text{O}$ ) of sulfate in desert varnish demonstrate that atmospheric deposition of dust is an important component of the varnish formation process [2]. A 2017 study of architectural rock varnish determined that vehicle emissions are a likely source of Mn [3]. In this study, we evaluate airborne dust as a potential Mn source at a location where rock varnish is actively forming.

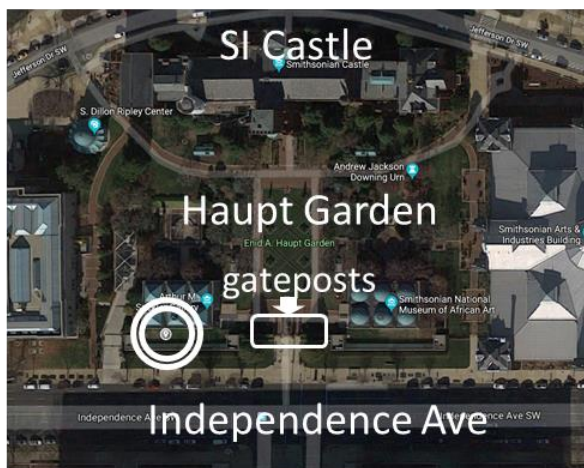
Urban dust samples were collected on polycarbonate filters using a portable sampler (Hi-Q Environmental Products, Model PSU-2-GN) [4] with a size selective inlet (10  $\mu\text{m}$  particle diameter size cut-off, URG). The collection times were 24 hours, and the volumetric flow rate was 30 L/min. Samples were collected near the Haupt Garden gateposts and heavily trafficked Independence Ave. (Fig. 1). A TESCAN MIRA3 and a 20 keV/1 nA electron beam and  $4 \times 30 \text{ mm}^2$  PulseTor silicon drift detectors (SDD) were used to analyze particles. Automated analysis was performed using the SEMantics extension to NIST DTSA-II [5]. The sum of the 4 SDD spectra (dwell time of 400 ms per spectrum) were used for quantification using NIST Graf [6]. A novel algorithm was then used to cluster the data obtained for 39,491 particles [7]. Data were then reprocessed using a manually developed rule set.

Table 1 lists the major particle classes representing  $\approx 92\%$  of the particle population. Figure 2 shows representative elemental signatures of the four major particle classes: silicate, Fe oxide, vehicle-related and CaMg carbonate. Only 52 out of  $\approx 40\text{K}$  particles had elevated levels of Mn ( $\geq 10 \text{ wt } \%$ ). Overall, our results show low, but detectable levels of Mn in the atmosphere in the Castle area. Efforts are underway to estimate the mass of Mn transported by atmospheric dust deposition for particles under 10  $\mu\text{m}$  in size. To our knowledge, this is the first study to examine the linkage between individual particle analysis of dust and active rock varnish formation.

### References:

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- [2] Bao, H., Michalski, G.M. and Thiemens, M.H, *Geochimica et Cosmochimica Acta* **65** (2000), 2029.
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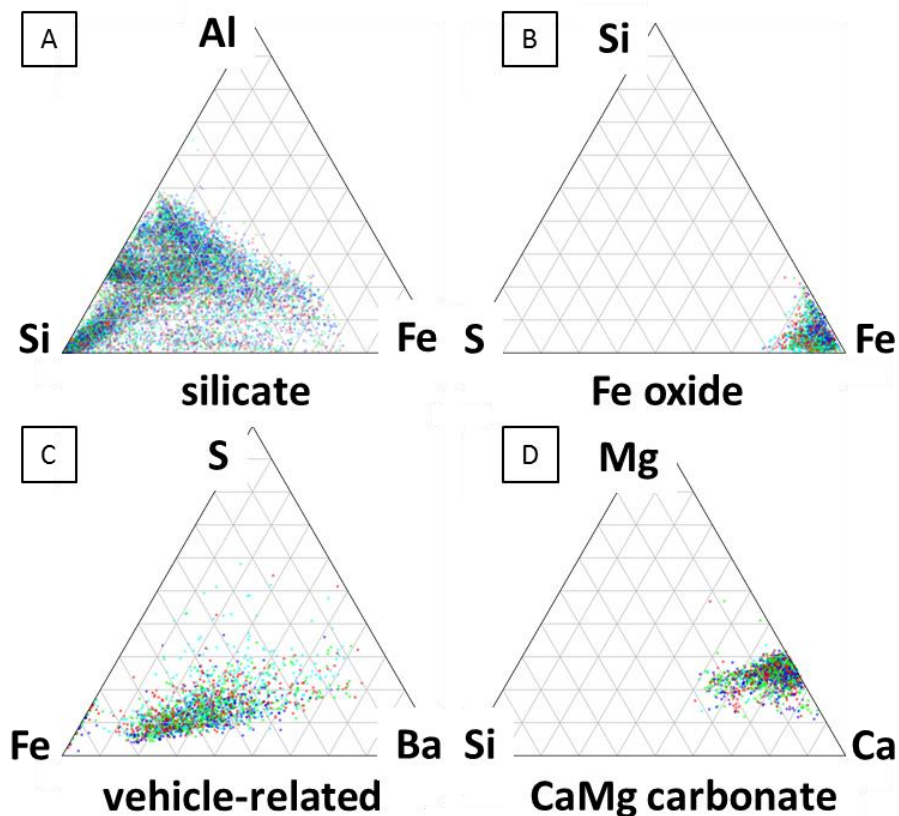
[7] Ritchie, N.W., *Microscopy and Microanalysis* 21(5) (2015), 1173.



**Figure 1.** Plan view of the Smithsonian Institution Building (SI Castle), Enid A. Haupt Garden gateposts (white rectangle), Independence SW Ave., and dust collection site (nested white circles) in Washington, DC, USA.

**Table 1.** Major particle classes ranked by count fraction of 39,491 particles. ( $\approx 92\%$  of particle population)

Rank	Class name	Count	Fraction (%)
1	silicate	16,868	40.7
2	Fe oxide	10,141	25.7
3	vehicle-related	2,455	6.2
4	CaMg carbonate	1,912	4.8
5	Fe(Mn) oxide	1,341	3.4
6	Ca carbonate	1,287	3.3
7	Fe oxide + silicate	1,192	3.0
8	Ca sulfate	970	2.5
9	Fe sulfide	760	1.9



**Figure 2.** Elemental signatures for major particle classes by weight fraction of ternary end-members. A) silicate. B) Fe oxide. C) vehicle-related (Fe-Ba-S-Cu-Si-Sb-Zr). and D) CaMg carbonate.